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Study of Properties of PVC Used in the Production of Artificial Skins Obtained with Additives on the Basis of Metal Salts

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ABSTRACT: In the article, the authors describe a method for obtaining a stabilizer based on local recycled materials - PET. In addition, IR analyzes are made, as well as thermogravimetric analysis of PVC compositions using metal phthalates, their graphs are presented, and conclusions are drawn on the material obtained. Also in the article, the authors carried out a literary review on the current state of the receipt of additives, namely, stabilizers for PVC, which are used for the production of artificial leather.

KEYWORDS: artificial leather, polyvinyl chloride (PVC), additives, stabilizers, polyethylene terephthalate (PET), destruction, IR spectroscopy, analysis, thermogravimetric analysis, destruction, metal phthalates.

I. INTRODUCTION

At the present stage of production, synthetic leather is a material consisting of several layers and inclusions of various origins. The presence of polymers in the composition of the material provides an imitation of the structure, features, and technological properties of natural leather.

A huge variety of polymer coatings, depending on the purpose, are produced from an even more diverse raw material, which differs in the chemical nature and structure of polymers (Polyvinyl chloride (PVC), synthetic rubbers, polyamides, polyacrylates, polyurethanes, etc.).

Polyvinyl chloride itself is a rather tough substance, and all kinds of special fillers and additives are added to soften it. In the process of using the material, many of them gradually evaporate, giving an unpleasant chemical smell to PVC leatherette. In addition, the material changes its quality characteristics - it becomes brittle, brittle, especially at low temperatures (from -10 degrees), changes its aesthetics. To obtain a high-quality leather material identical to natural, it must be properly filled, depending on the purpose, with various additives, plasticizers, stabilizers, etc.

Polyvinyl chloride is the basis for a wide range of materials that are used in almost all industries, these are vinyl plastics, soft elastic compounds, finishing materials, insulating materials, and this list can be continued for quite some time. Suspension, microsuspension, emulsion and mass grades of polyvinyl chloride largely determine the variety of properties of materials from it, however, it should be noted that in addition to the production method of PVC itself, there is also a wide range of additives of various nature, including both fillers of a polymeric and monomeric nature.

Among thermoplastics, polyvinyl chloride has no analogues in terms of the number of components in the composition and can only be compared with rubber. The composition of the mixture of such a composition, which includes more than a dozen components, can be explained by the specifics of the polyvinyl chloride itself. The main

physicochemical characteristics of polyvinyl chloride are rather low temperatures of the onset of its decomposition, as well as the mechanism of thermal degradation inherent only for PVC.

Aging of the polymer occurs as a result of changes occurring in it, which ultimately lead to a decrease in quality and a decrease in the service life of the material.

Temperature, various mechanical loads, oxidizing agents, radiation, and some act simultaneously - all this can become a factor for the aging of polymers. The greatest destructive effect on the polymer is the so-called thermo-oxidative destruction, when the destruction of the material proceeds under the influence of temperature and oxygen [1].

The most commonly used plasticizers are dialkylortho-phthalate esters. Alcohols are taken from the range from hexyl (C6) to tridecyl (C13) and can be either linear or branched. It should be borne in mind that with an increase in the degree of branching of alcohol, the ability of the plasticizer to volatility and susceptibility to oxidation increases. However, it can withstand low temperatures in PVC while having a higher volume resistivity in PVC blends. A plasticizer that has been adopted as a general-purpose industry standard is phthalic acid diethyl 2-hexyl ester known as DEHP or DOP. With its help, all other dialkyl phthalates and PVC plasticizers are compared for the efficiency factor (FE) [2].

In order to prevent aging of polymers, various fillers are added to their composition, which stabilize the chemical and thermal stability of the polymer. When using stabilizers of this kind, the finished product significantly increases resistance to external influences, and also, which is important, increases their service life.

The effectiveness of the stabilizer determines the amount added to the polymer composition. In addition, there is the fact that some of them have side effects on the properties of the polymer itself. The optimal ratio of the stabilizer to the weight of the composition is 5–95%. In industry, stabilizers are added in an amount up to 5% by weight of the composition. According to the protective effect, stabilizers can be divided into: antioxidants, antiozonants, light stabilizers.

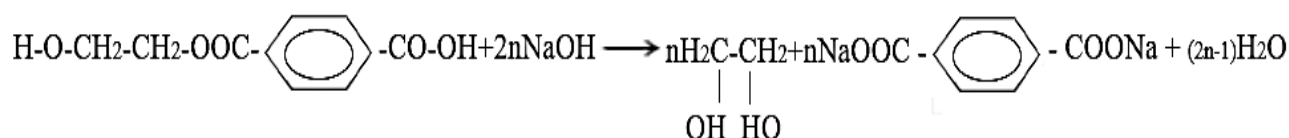
As a rule, a complex mixture of stabilizers is used to impart properties of a certain character to the polymer.

An ideal stabilizer should provide:

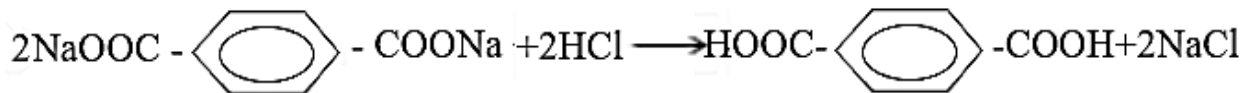
- inhibition of dehydrochlorination, oxidation, rupture and cross-linking of macromolecules, formation of polyene sequences;
- suppression or weakening of the processes of destruction of macromolecules, catalyzed by various chemical agents;
- high compatibility with the polymer composition;
- easy plasticization and optimal melt viscosity;
- lubricating effect;
- lack of smell;
- weather and heat resistance;
- bacteriological and chemical resistance;
- resistance to radiation of various types;
- stability of the initial color [3].

II. MATERIALS AND METHODS

The range of additives produced in our country and containing such a complex of properties is rather limited, therefore, additives of foreign origin are mainly supplied to the domestic market. The task of creating multifunctional stabilizers that provide the required stabilization and processing is one of the priorities in this direction.

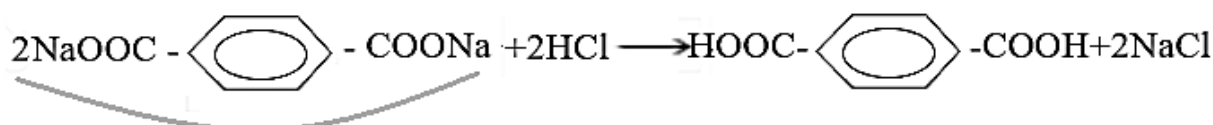


To synthesize a stabilizer based on metal-containing compounds for PVC leatherette, the authors used the disodium salt of terephthalic acid. The latter was obtained by the destruction of secondary PET. For this, secondary PET in the form of flakes, crushed to a size of 3-5 mm², was heated at a temperature of 140° C in the presence of sodium hydroxide. The foam that forms on the surface of the boiling mixture indicates the beginning of destruction. It should be noted that when the temperature rises to 180° C, the process proceeds more intensively.



To obtain terephthalic acid, the resulting mixture was neutralized with HCl, then the precipitate was filtered with a vacuum pump and washed with distilled water.

However, in this case, we need the intermediate terephthalic acid disodium salt.



When an aqueous solution of metal acetate was added to an aqueous solution of the disodium salt of terephthalic acid, a pronounced precipitation of the metal salt was observed, which was subsequently filtered using a vacuum pump. The filtrate was washed several times with distilled water.

The resulting substance (AC-1) was used in the production of PVC with various stabilizer ratios. Subsequently, IR analyzes of the samples were carried out, the graphs of which are given below.

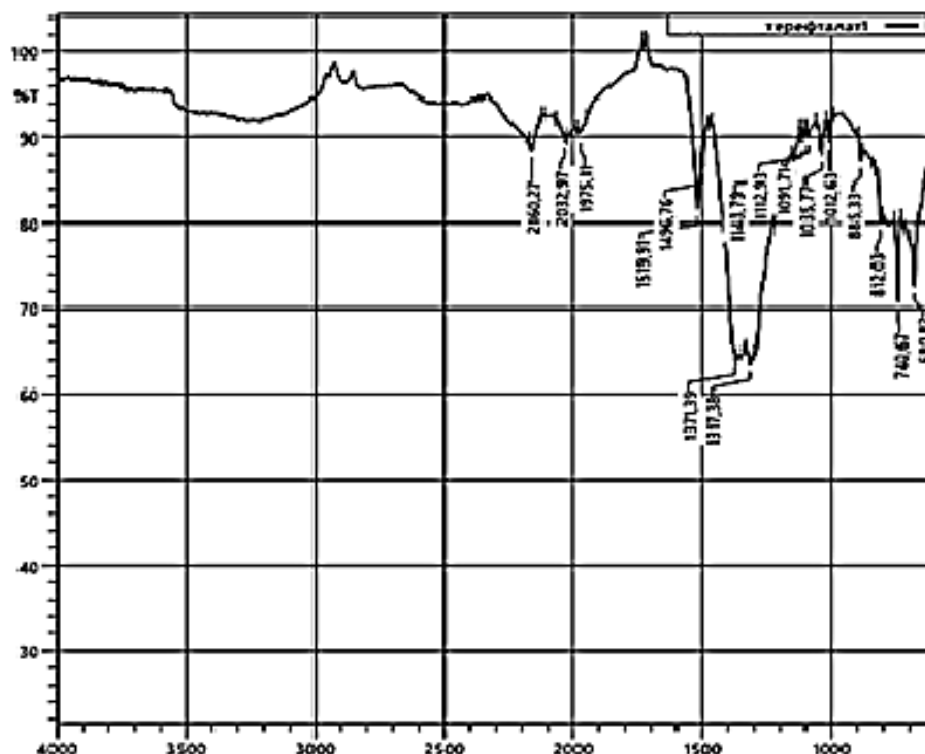


Fig. 1. IR spectrum plot of the obtained metal-containing stabilizer

The resulting stabilizer AC-1 was introduced into the composition immediately before heating. The optimum temperature for heating the composite mixture was 170-200° C, and the mixture should be stirred continuously. The

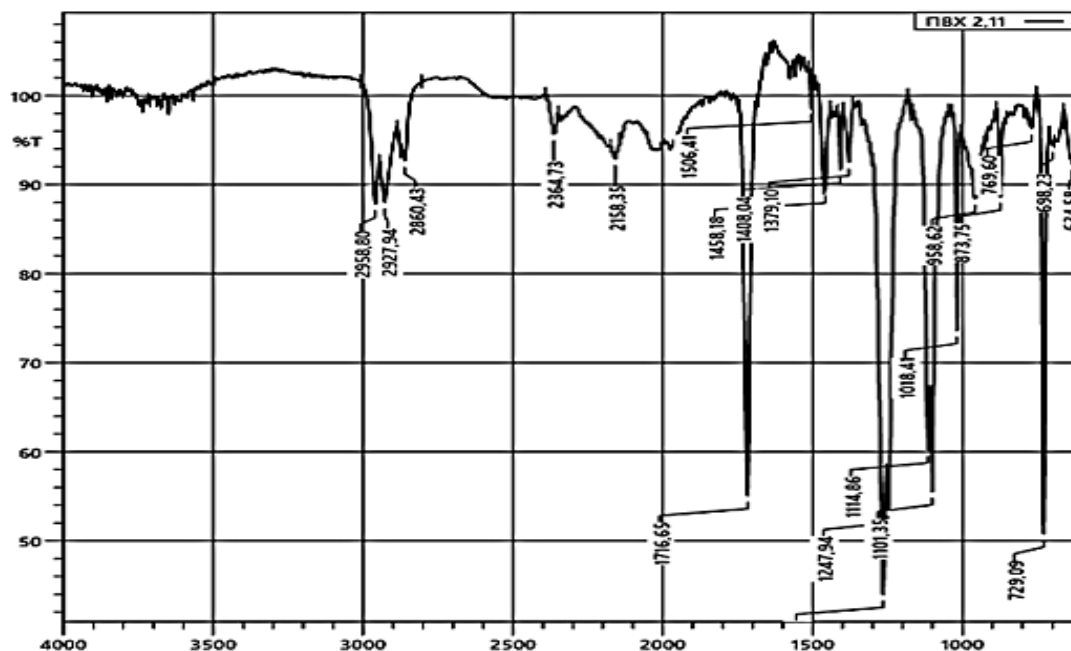


Fig. 2. The graph of the IR spectrum of the obtained sample No. 1

dosage can be up to 15%, but as a rule, 02-3% by weight of the composition is usually used.

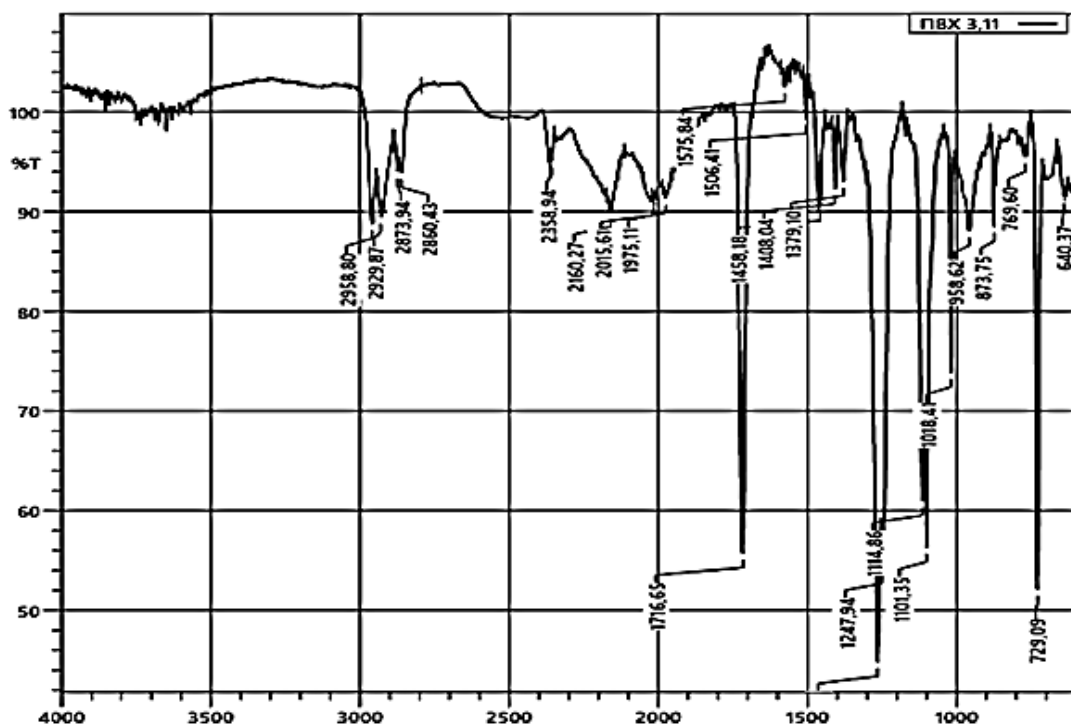


Fig. 3. The graph of the IR spectrum of the obtained sample No. 2

III. RESULTS

The graphs of the differential thermal and thermogravimetric analyzes of the samples were obtained on a SHIMADZU synchronous thermal analyzer of the DTG-60 series.

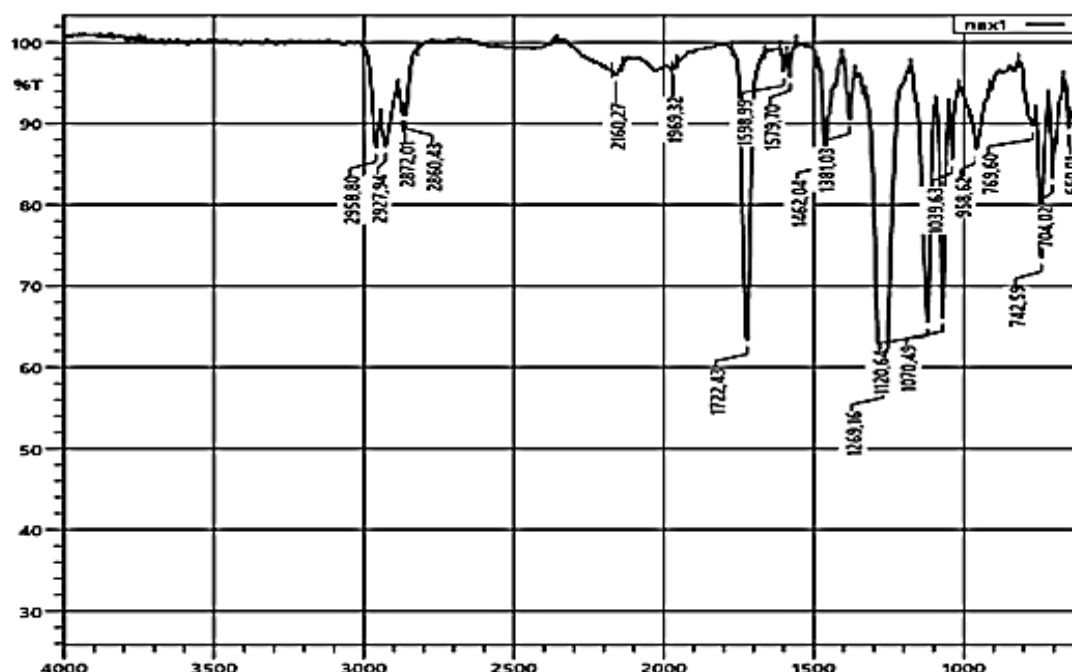


Fig. 4. The graph of the IR spectrum of the obtained sample No. 3

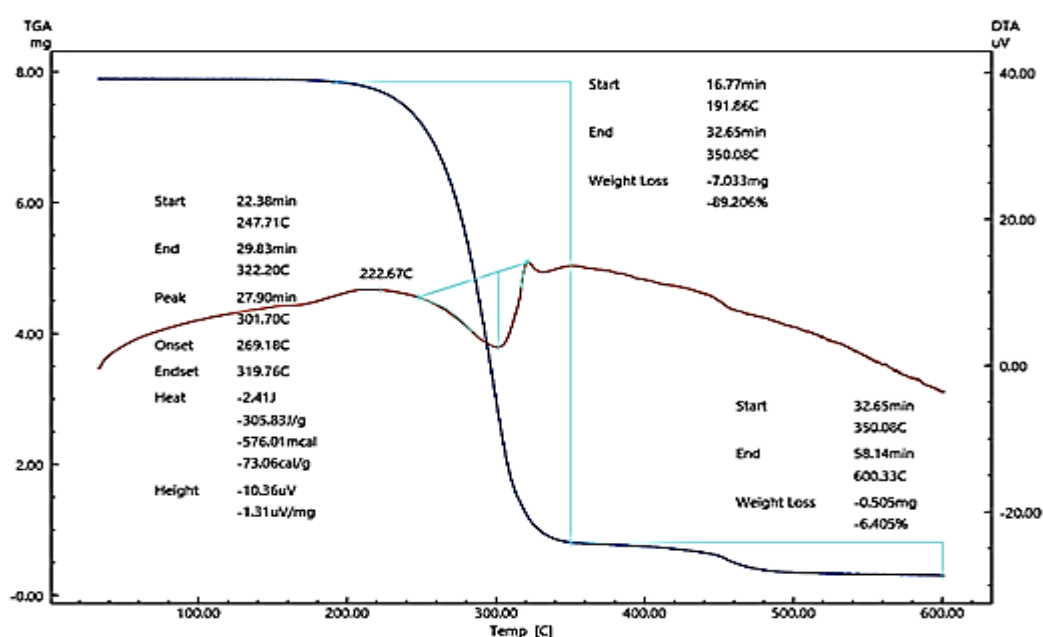


Fig. 5. Schedule of thermal destruction of PVC depending on time and temperature (sample No. 1)

It is clearly seen from the TGA graph (blue in the figure) of sample No. 1 that the main changes in the sample fall on the 16th minute of analysis, where, starting from a temperature of 191,8°C, there is a sharp loss of sample mass – 89,2% within 15,8 minutes, which corresponds to 7,03 mg of the total weight of the sample. Starting from a

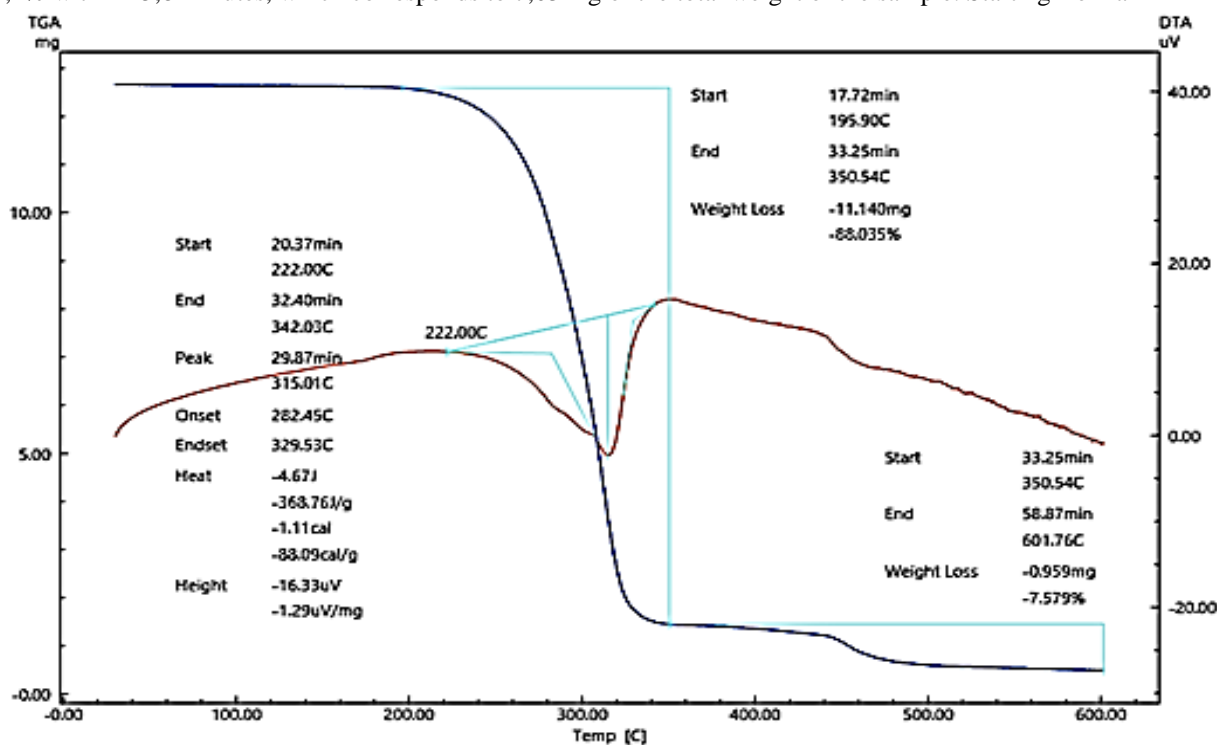


Fig. 6. Schedule of thermal destruction of PVC depending on time and temperature (sample No. 2)

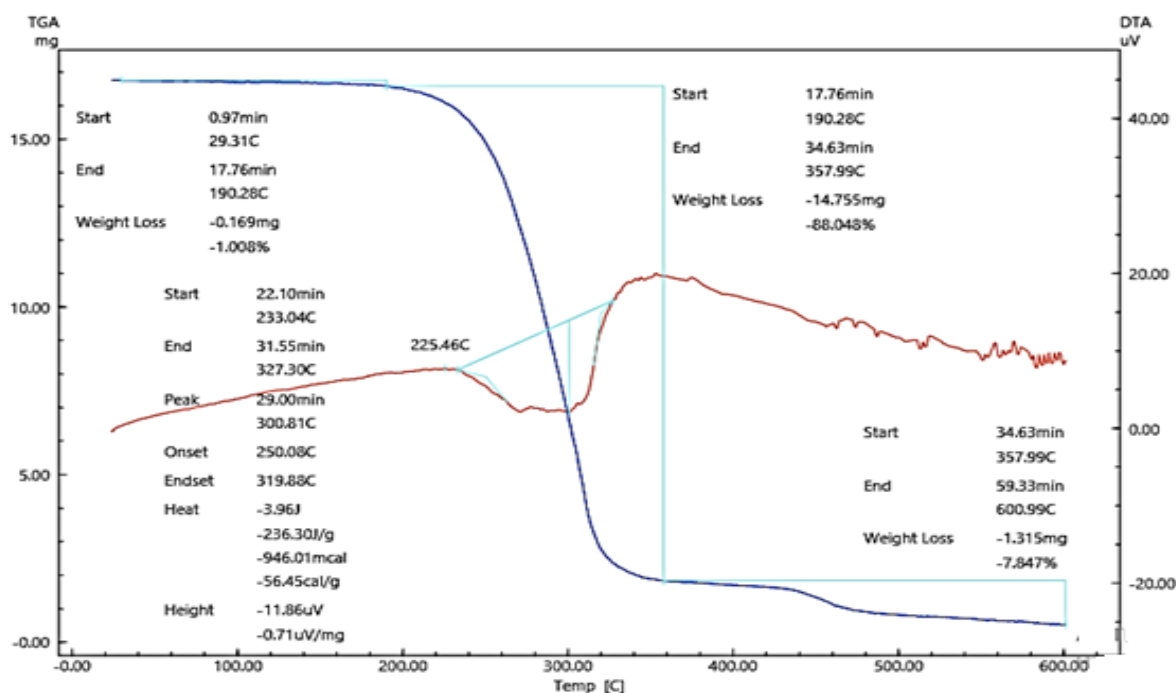


Fig. 7. Schedule of thermal destruction of PVC depending on time and temperature (sample No. 3)

temperature of 350°C, corresponding to 32 minutes of analysis, the sample weight is lost more steadily, i.e. in 25,5 minutes 6,4%, which corresponds to 0.5 mg of the weight of the remaining sample.

Changes take place starting from 16.7 minutes, when sample No. 2 loses mass at 195.9 °C. More significant losses are observed starting from 230°C, sample No. 2 abruptly loses about 88% of its mass, within 14 minutes, which corresponds to 11.14 mg relative to the mass of the sample taken. Starting at 340 °C and above, the sample used loses mass more steadily, i.e. within 25 minutes about 76% of the weight of the remaining sample. Summing up, we can say that the obtained sample No. 2 can easily withstand temperatures up to 230°C.

As can be seen from the graph, changes occur starting from 17.7 minutes, when sample No. 3 loses in mass at 190.28 °C. More significant losses are observed starting from 240 °C, sample No. 3 abruptly loses about 88% of its mass, within 14 minutes, which corresponds to 14.75 mgr relative to the mass of the sample taken. Starting from a temperature of 357 °C and above, it cannot be said that the sample used loses mass more stably, for example, at a temperature of 460 °C, you can notice a small jump, then the mass loss is more stable.

IV. DISCUSSION

As a rule, such substances have a powdery consistency, white and light tones, and dissolve in inorganic acids. Insoluble in water and organic solvents. An important parameter is heat resistance.

If the parameters of the process of obtaining the composition are not observed, a sharp decrease in the quality of the product is observed, which manifests itself in color, texture, elasticity, etc.

From the graphs of the IR spectra of the tested samples, it can be seen that relative to sample No. 3 (without the addition of AC-1), samples No. 1 and No. 2 (with the addition of AC-1) do not undergo a noticeable change, no strong deviations of the peaks are observed, from which one can make the conclusion that the metal-containing stabilizer does not adversely affect samples No. 1 and No. 2.

When comparing graphs No. 1 and No. 2 of TG analysis samples, no noticeable changes are observed, however, sample No. 2 in the last period of time loses more mass in the same time as sample No. 1. Summing up the TG graphs of the obtained samples, we can conclude that sample No. 3 is less resistant to a given temperature and loses more in mass than No. 1 and No. 2.

V. CONCLUSION

As you know, unstabilized PVC has high chemical and low thermal stability; it decomposes at the processing temperature with the release of hydrogen chloride. It becomes obvious that for the plasticization process of PVC when exposed to mechanical energy, a sufficiently good stabilization is required.

Recycling of PET is also one of the most pressing issues of today's ecology. The use of such waste has become a priority in the chemical industry.

Thus, from local secondary waste, the authors obtained an additive to the PVC composition used in the production of leatherette. From the graphs of the obtained IR analysis, it was found that AC-1 did not have a significant effect on the structure of PVC compositions. The main property of AC-1 is to increase the thermal stability of the obtained PVC composition, which will be described in the following works of the authors

VI. ACKNOWLEDGEMENT

There is a method for alkaline hydrolysis of PET waste to obtain terephthalic acid, including hydrolysis of PET with sodium hydroxide in a solvent when heated, followed by adding water to the reaction mass until the resulting disodium salt of terephthalic acid is completely dissolved, separating the aqueous layer from the solvent, precipitating terephthalic acid from an aqueous solution of concentrated hydrochloric acid followed by filtration, washing and drying of terephthalic acid [4].

A known method of obtaining a polymer composition for artificial skin, including suspension polyvinyl chloride, dioctyl phthalate, dioctylsebacate, calcium stearate, cadmium stearate, epoxidized soybean oil, stearic acid and a filler, characterized in that, in order to reduce the stickiness of the artificial skin and increase the adhesive capacity, the composition contains wastes of grinding synthetic leather of the coagulation method of production [5].

Analyzing the work of scientists on the production of PVC and the processing of secondary polymers, we can conclude that the topic has not been sufficiently studied and the improvement of these processes is one of the priority directions in science.



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